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#### READY-TO-FILL PLASTIC SAUSAGE SKIN

This invention relates to a gathered, multilayer, biaxially oriented, shrinkable, polyamide-based tubular film conditioned in ready-to-fill form for wrapping fillings which are packaged in liquid or pasty state, preferably for sausage meat.

Developments relating to synthetic sausage casings are characterised by the desire to provide products which meet the changing demands of the meat processing industry with regard to economic and environmental factors.

Multilayer, biaxially oriented plastic casings based on polyamide (PA) in conjunction with other plastics have for many years in many respects proved successful for the production of boiled and boiling sausages.

The person skilled in the art takes biaxial orientation to mean the transverse and longitudinal stretching of the thermoplastic extrudate at temperatures between the glass transition temperature and melting temperature of the polymeric materials. Biaxial orientation is conventionally performed by means of a bubble filled with a gas or fluid pressure cushion enclosed between two gas- or fluid-tight roller pairs running at different peripheral speeds. During orientation, the molecules of the tubular film, which is in the solid state, become aligned in such a manner that the modulus of elasticity and strength in both the transverse and longitudinal direction are considerably increased. Orientation is generally followed by a further heat treatment.

DE 4,339,337 describes a five-layer, biaxially oriented tubular film for packaging and wrapping foodstuffs. This casing is characterised in that it is made from an internal and external layer of the same polyamide

material and a central polyolefin layer together with two coupling layers consisting of the same material.

EP 530 538 describes a five-layer, coextruded, biaxially oriented tubular film having at least 3 polyamide layers, wherein polymer layers having barrier properties for water and oxygen are arranged between the inner and outer polyamide layers.

Highly efficient processing of, for example, the above-stated tubular films is of particular interest to the meat processing industry. The tubular films are accordingly subjected to a gathering process in which they are folded together on a gathering mandrel to form a gathered "caterpillar", so dramatically reducing the length of the gathered tube. Gathering of a tubular material is known, for example, from DE 89 44 623 C2.

The flexibility of the polyamide-based tubular films in the dry state is insufficient for them to be filled without creases and to be applied so as to retain sufficient shrinkage properties after the boiling or cooking operation, such that a smooth, crease-free sausage is obtained. For this reason, the tubular polyamide film is dipped in or rinsed with cold and also hot water shortly before filling with meat. This procedure is described *inter alia* in DE 3 426 723

EP 0 248 860 describes that the gathered tubular films exhibit variable water absorption on rinsing with water, for example due to differing application rates of gathering lubricant, so giving rise to differing levels of elasticity of the tubular film within the "caterpillar", which is also accompanied by variations in diameter on filling. For this reason, the tubular film is premoistened before gathering by rolling the tubular film with an internal bubble of water. This has the disadvantage of non-uniform moistening over the length of the roll, as the quantity of water decreases with the length of the roll.

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EP 0 640 289 describes a gathered footstuff casing conditioned in ready-to-fill form which, on gathering, is sprayed with a mixture (emulsion) of water and gathering lubricant, wherein production and ensuring uniformity of spraying properties are particularly problematic.

EP 0 815 732 describes a ready-to-fill sausage skin which, before gathering, is sprayed with a spraying solution which, together with an emulsifier, comprises a substance to establish the pH value, for example potassium sorbate, a bactericide and a lubricant. The complicated production process for the emulsion may be considered a disadvantage.

The object thus arose of providing a ready-to-fill, gathered tubular film having a large compression ratio, which film is simply conditioned in such a manner that it need not be additionally rinsed by the user and retains elevated consistency in diameter during the filling process and reliable machinability.

This object was achieved by the provision of a tubular film which is biaxially oriented, has at least three layers, is shrinkable and has polyamide-based layers on both sides (inside and outside) and a water barrier layer in the middle, may optionally preferably have between the inner layer and/or outer layer and central layer one or also more further layer(s) and is conditioned in ready-to-fill form by means of prior spray mositening and gathering.

Accordingly, in one aspect the present invention provides a gathered, biaxially oriented, shrinkable tubular film laminate conditioned in ready-to-fill form, comprising an outside film, an inside film and at least one water barrier layer interposed therebetween, wherein said outside film and said inside film are polyamide-based characterized in that said outside film contains a spraying medium in an amount corresponding to the saturation limit thereof.

In another aspect the invention provides a process for making a gathered film laminate comprising (i) preparing a biaxially oriented, shrinkable tubular film laminate, and (ii) spraying on said laminate a spraying medium, and (iii)

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gathering said tubular film laminate, and (iv) storing said gathered tubular film laminate under conditions sufficient to promote the soaking of said spraying medium into the outer layer.

Owing to specific spray moistening conditions and a simply prepared spraying agent, the tubular films according to the invention have surprisingly been found to provide excellent processing characteristics on gathering and filling in the case of the preferred use as a synthetic sausage skin.

Spray moistening is performed according to the invention by applying the spraying medium used for moistening, preferabl water, which may optionally additionally contain a conventional fungicide (for

example quaternary ammonium chloride compounds as are offered for sale by Bode Chemie under the commercial name

Sokrena) and/or conventional preservatives (for example sodium salts, manufacturer: Merck), preferably at a droplet size of 0.01 to 0.5 mm, preferably of 0.05 to 0.1 mm, on the outside, preferably on both sides of the collapsed tubular film as it passes through a conventional commercial winding machine (for example supplied by Küko or Eichel). The quantity of the spraying medium applied in this operation is established, preferably by the arrangement of the spraying apparatus and the speed of the rolling operation, such that the quantity of spraying agent applied at most corresponds to the saturation limit of the outer polyamide layer. In another, specific embodiment of the invention, in addition to the application of the spraying agent, gathering lubricants, for example triglyceride mixtures, may simultaneously be transferred onto the tubular film in the same operation using a further apparatus.

The rolled tubular film is subsequently preferably stored in the rolled state in a manner that permits no exchange of moisture with the surroundings, for example in a polyethylene pouch having a wall thickness of approx.  $100~\mu m$ , until the spraying medium has soaked in to such an extent that no liquid droplets are any longer visible on the surface. The storage time required for this purpose is generally at least 24 hours.

The tubular film moistened according to the invention may be gathered with a much higher compression ratio than unmoistened tubular film. The compression ratio, *i.e.* the ratio of the gathering length of the ungathered tubular film to the length of the gathered "caterpillar" may be increased from <50 to greater than 100. Moreover, both in the unfilled and filled state, virtually no gathering creases are any longer visible or detectable as surface markings, wherein the improvement is achieved both with axial gathering and helical gathering. The consistency in

diameter of the filled sausage is distinctly increased and filling may be performed on automatic filling machinery in a substantially more troublefree manner.

The polyamide based layers of the tubular films according to the invention preferably contain as the substantial constituent a linear aliphatic polyamide (PA) selected from among PA 6, PA 66, PA 11, PA 12, and/or linear, aliphatic copolyamide, selected from among PA 6,66, PA 4,6, PA 6,6, PA 6,8, PA 6,9, PA 6,10, PA 6,11, PA 6,12 or a blend of the above-stated polyamides and/or copolyamides, and may additionally contain conventional auxiliary substances in conventional quantities. Proportions of aromatic polyamide or partially aromatic polyamide may be incorporated into the polyamide, copolyamide or blends, for example in order to improve the processing or the barrier properties of the casing. Tubular films, in particular synthetic sausage skins, which are suitable for the production of the gathered tubular films conditioned in ready-to-film form according to the invention are commercially available under the name Walsroder® K flex or Walsroder® K plus (Wolff Walsrode AG).

The water barrier layer in the middle and optionally further water barrier layers preferably substantially consist of one or more polyolefins having water vapour barrier properties, such as in particular polyethylene or polypropylene or polybutene or the copolymers thereof, which may additionally have modified terminal groups in order to improve composite adhesion, or also contain so-called ionomer polymers, such as in particular Zn ionomers prepared from ethylene/acrylic acid copolymers and may additionally contain conventional auxiliary substances in conventional quantities.

In order to reduce greying effects and in order to improve the shelf life of the finished sausages, the tubular films may, apart from the water barrier layer, additionally contain at least one further layer having oxygen barrier properties. These oxygen barrier layers preferably substantially consist of saponified ethylene vinyl acetate or blends thereof with other polymers.

### Examples & Comparative Examples

The tests listed below were performed with the following Examples: Compression ratio Unit (m/m)

As mentioned above, the compression ratio is the ratio of the length of the gathered sausage skin before gathering to the length of the gathered "caterpillar" at a given gathering tube diameter. For example, with a 60 mm diameter sausage skin, 40 mm gathering mandrel, length of gathered sausage skin = 30 m and length of gathered "caterpillar" = 0.42 m, the compression ratio is 30/0.42 m/m = 71 m/m.

### Flexural rigidity

Flexural rigidity is taken to mean the force with which the gathered "caterpillar" resists being changed from its straight shape into a bent or other shape deviating from the straight shape. This test may advantageously only be used with helical gathering. A quality rating on a scale of 1 to 5 is awarded, with 1 meaning a large force and 5 meaning very little force.

## Evaluation of gathering creases (roughness of finished sausage)

The extreme mechanical loads to which the sausage skin is exposed during the gathering process result in the formation of gathering creases, which may sometimes still be seen on the finished sausage. Evaluation was performed on a scale from 1 = no visible gathering crease marks to 5 = severe gathering crease marks.

### Consistency of diameter

The geometric uniformity of the sausage products, which may inter alia be determined by a uniform diameter of the products, is of great importance to industrial users. Evaluation was performed using a scale

from 1 =  $\pm$  0.1 mm tolerance in diameter to 5 =  $\pm$  0.5 mm tolerance in diameter, wherein the diameter was measured in the middle of the sausages, which were approx. 25 cm in length.

# Filling behaviour

Filling behaviour is taken to mean the reliability with which the sausage skin may be filled without bursting or other defects. Evaluation was performed using a rating scale from 1 = no defects within 100 "caterpillars" to 5 = at least 5 defects within 100 "caterpillars".

## **EXAMPLES**

The following Examples and Comparative Examples are intended to illustrate the invention.

The various polymers used in the casings produced according to the invention and in the Comparative Examples are abbreviated as follows:

PA	Polyamide 6	e.g. Durethan B 40 F (Bayer AG)
PO-HV	Propylene-based copolymer coupling agent	e.g. Bynel E 379 (DuPont)
XX	Ethylene/vinyl alcohol copolymer	e.g. EVAL LC F 101 BZ (Kuraray)
aPA	Partially aromatic copolyamide	e.g. Selar PA 3426 (DuPont)
МВ	Polyamide 6-based masterbatch	e.g. coloured masterbatch PA gold

### Example 1 (B1):

The commercial product Walsroder® K plus SK, nominal diameter 60 mm (manufacturer: Wolff Walsrode AG, Walsrode) is spray moistened according to the invention with a total weight gain of 8% and, after a waiting period of 24 hours, 50 m are gathered with a gathering lubricant on an axial gathering machine with a gathering tube diameter of 40 mm to a "caterpillar" length of 420 mm. This sausage skin was filled without further rinsing.

### Comparative Example 1.1. (VB1.1):

25 m of the sausage skin used in Example 1 are gathered without moistening with a gathering lubricant on an axial gathering machine with a gathering tube diameter of 40 mm to a "caterpillar" length of 420 mm.

The sausage skin was rinsed in accordance with the manufacturer's instructions (for example 30 minutes in hand hot water) and filled.

Example 2 (B2):

The commercial product Walsroder® K flex red, nominal diameter 60 mm (manufacturer: Wolff Walsrode AG, Walsrode) is spray moistened according to the invention with a total weight gain of 6% and, after a waiting period of 24 hours, 60 m are gathered with a gathering lubricant on a helical gathering machine with a gathering tube diameter of 40 mm to a "caterpillar" length of 420 mm. This sausage skin was filled without further rinsing.

### Comparative Example 2 (VB2):

25 m of the sausage skin used in Example 2 are gathered without moistening with a gathering lubricant on a helical gathering machine with a gathering tube diameter of 40 mm to a "caterpillar" length of 420 mm.

The sausage skin was rinsed in accordance with the manufacturer's instructions (for example 30 minutes in hand hot water) and filled.

Comparative Example 3 (VB3.1):

A three-layer plastic sausage skin was produced by the tubular film orientation process. The sausage skin had a nominal diameter of 60 mm and a total thickness of 45 mm.

The layer structure is: (inside) PA / copolyamide / PA (outside)

Thickness profile: (µm) (inside) 10 / 10 / 25 (outside)

This sausage skin is spray moistened as described as above with a total weight gain of 6% and, after a waiting period of 24 hours, 60 m are gathered with a gathering lubricant on an axial gathering machine with a gathering tube diameter of 40 mm to a "caterpillar" length of 420 mm. This sausage skin was filled without further rinsing.

### Comparative Example 3 (VB3.2):

As in VB3.1, but 30 m are gathered in an unmoistened state to a "caterpillar" length of 420 mm and rinsed for 30 minutes before filling. Example 4 (B4):

A five-layer plastic sausage skin was produced by the tubular film orientation process. The sausage skin had a nominal diameter of 60 mm and a total thickness of 55 µm.

The layer structure is: (inside) P

(inside) PA / PA+MB+aPA / PO-HV /

PA+MB+aPA / PA (outside)

Thickness profile: (µm) (inside) 5 / 20 / 5 / 20 / 5 (outside)

This sausage skin is spray moistened according to the invention with a total weight gain of 6% and, after a waiting period of 24 hours, 60 m are gathered with a gathering lubricant on an axial gathering machine with a gathering tube diameter of 40 mm to a "caterpillar" length of 420 mm. This sausage skin was filled without further rinsing.

### Example 5:

A five-layer plastic sausage skin was produced by the tubular film orientation process. The sausage skin had a nominal diameter of 60 mm and a total thickness of 41 µm.

The layer structure is: (inside) PA / PO-HV / XX / PA+aPA /

PA+MB (outside)

Thickness profile: (µm) (inside) 8 / 4 / 3 / 20 / 6 (outside)

This sausage skin is spray moistened according to the invention with a total weight gain of 6% and, after a waiting period of 24 hours, 50 m are gathered with a gathering lubricant on an axial gathering machine with a gathering tube diameter of 40 mm to a "caterpillar" length of 420 mm. This sausage skin was filled without further rinsing.

The following Table shows the test results:

Sample		B1	VB1.1	B2	VB2	VB3.1	VB3.2	B4	B5
Nominal diameter		60	60	60	60	60	60	60	60
Compression ratio on gathering	(m/m)	119	60	143	60	143	71	143	119
Flexural rigidity of gathered "caterpillar"	Rating	-	-	1	5	-	-	-	-
Evaluation of gathering creases (roughness) in filled state	Rating	1	4	1	3	4	3	1	1
Filled diameter	mm	62	62	62	62	62	62	62	62
Consistency of sausage diameter	Rating	1	4	1	3	3	3	1	1
Filling behaviour on filling machine	Rating	1	4	1	4	4	1	2	1

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.